# Improved cyclability of Na-birnessite partially substituted by cobalt

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## Abstract

We measured the electrode performance of Na-birnessite, which is layered manganese dioxide with sodium ions and water in the interlayer, for use in rechargeable lithium batteries. We focused on the effects of water on the electrode performance. X-ray diffraction (XRD) measurement and thermogravimetric (TG) analysis indicated that the weight loss on heating the material at 100 °C corresponded to the removal of surface water with no structural change, while that at 150 °C was associated with the removal of lattice water, leading to the layer shrinkage. According to this result, we prepared three kinds of electrode samples with different drying conditions, and examined the effect on the electrode performance. Furthermore, to improve the cyclability, we synthesized samples in which cobalt was substituted for some of the manganese. Even with a large substitution ratio of over 30%, we obtained the same initial capacity as the non-substituted sample, and the cyclability was improved. We assume that the substituted cobalt fixed sodium ions in the interlayer in the form of pillars that stabilized the layer structure. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Manganese dioxide; Birnessite; Rechargeable lithium battery; Drying condition; Cyclability; Substitution

## 1. Introduction

Birnessite is a type of manganese dioxide, which has a layer structure with water and alkali ions in the interlayer as shown in Fig. 1. This compound is interesting for use as a positive electrode material for rechargeable lithium batteries because manganese dioxides are less expensive, more abundant and generally have higher thermal stability than $LiCoO_2$ that is used in commercially available lithium ion batteries. Indeed, it is known that birnessite has a large discharge capacity in the 3 V region. For example, Strobel and Mouget [1] and Bach et al. [2,3] have reported that Na-birnessite (birnessite with $Na^+$ in the interlayer) and SG-birnessite (birnessite without any alkaline ion in the interlayer, synthesized by the sol–gel method) have a first discharge capacity of 180 and 200 mAh g$^{-1}$, respectively, in the 2.0–4.0 V range.

As birnessite is a hydrated material, care must be taken when we use it as an electrode material for non-aqueous batteries. The water that is incorporated in the interlayer is called lattice water, and this is an important component of birnessite. Bach et al. have suggested that this lattice water ensures the elasticity of the layer structure and promotes the cycle life [2,3]. It has been also reported that excessive

drying leads to a small capacity due to the elimination of the lattice water [4]. In contrast, the use of birnessite without any drying process would contaminate the electrolyte by the protons/water, which could cause hydrogen to evolve on the negative electrode. However, there have been no reports detailing the effects of the drying conditions.

Furthermore, the cycling performance of birnessite was inadequate [1–3]. To improve the cyclability, Bach et al. [2] and Zhang et al. [5] have attempted to stabilize the layer structure by using pillared bismuth and vanadate ions, respectively. They succeed in improving the cyclability, but the resultant capacities are too small for practical use due to the heavy pillared ions. If we could fix lighter pillared ions in the interlayer, we can expect to improve the cyclability with large specific capacity.

As sodium is a light element, it has reported that Na-birnessite has a large specific capacity [1]. Furthermore, as sodium can be fixed more tightly in the interlayer than lithium [6], we can presumably use sodium ions as pillars to stabilize the layered structure. We assume that sodium is lost during the charging process when most manganese ions are oxidized to $Mn^{4+}$, and that substitution of a non-reactive element for manganese is effective to fix the sodium ions in the interlayer.

In this report, we selected Na-birnessite as the target compound, and focused on the drying conditions and metal substitution for manganese. We prepared three kinds of

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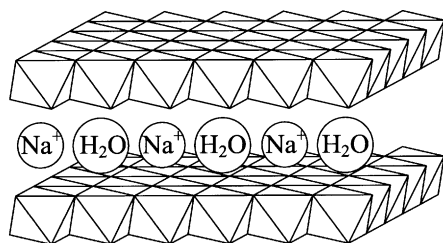*E-mail address:* tsuda@iba.iecl.ntt.co.jp (M. Tsuda).

Fig. 1. Crystal structure of Na-birnessite.

samples by using different drying conditions and observed the effects of water. To fix the sodium ions as pillars, we partially substituted cobalt for manganese. We expected the substituted cobalt, which exists as trivalent ions ($Co^{3+}$), to fix the sodium ions in the interlayer.

## 2. Experimental

We synthesized non-substituted Na-birnessite as follows [7]. We added 250 ml of 5.5 M (mol dm$^{-3}$) NaOH solution to 200 ml of 0.5 M $MnCl_2$ solution at 10 °C to form a white $Mn(OH)_2$ precipitate. We then bubbled oxygen into the $Mn(OH)_2$ precipitate at a rate of 5 l min$^{-1}$ for 5 h through a glass filter. After oxidation, the black Na-birnessite precipitate was filtered, washed with distilled water and then dried in air at 90 °C. We prepared cobalt substituted samples in a similar way, except that we used a mixture of $MnCl_2$ and $CoCl_2$ in various ratios as the starting material, instead of $MnCl_2$ alone. We synthesized the samples with cobalt substitution ratios of 0, 20, 30 and 40%. We call these samples, non-Co, 20-Co, 30-Co and 40-Co, respectively. We kept these samples in dry air because they are highly hygroscopic and absorb water in an ambient atmosphere.

We characterized the samples by X-ray diffraction (XRD) with Cu Kα radiation using a sealed sample holder with a polyimide window to avoid exposing the sample to the ambient atmosphere. We evaluated the chemical composition by using inductively coupled plasma emission (ICPE) spectroscopy and determined the manganese oxidation state by iodometry. We measured water removal/absorbance characters of the sample by thermogravimetry (TG).

We undertook electrochemical measurements using a coin cell with a metallic lithium negative electrode. The positive electrode mixture consisted of 70 wt.% manganese dioxide, 25 wt.% acetylene black as a conductive agent and 5 wt.% polytetrafluoroethylene as a binder. The electrolyte was a 1 M $LiPF_6$ solution in equal volumes of ethylene carbonate and dimethyl carbonate. We began the measurement from the discharging process, with a cell voltage of 2.0–4.0 V and a current density of 0.1 mA cm$^{-2}$ at room temperature.

We prepared three kinds of electrode pellets. The birnessite powder was first dried in air at 90 °C, and then it was kneaded in a dry atmosphere to form the electrode pellets. We call thus prepared pellets air dried (AD) samples. Some

pellets were further heated in a vacuum at 150 °C for 24 h. We denote them as vacuum dried (VD) samples. Other pellets were immersed in an electrolyte solution containing metallic lithium for 24 h. We call such samples electrolyte immersed (EI) samples. We stored these pellets in dry air before use as electrodes. We then examined the effects of the drying conditions on the cell performance.

## 3. Results and discussion

Table 1 shows the chemical composition of our Na-birnessite samples with and without cobalt substitution. We obtained the samples with an anticipatable amount of substituted cobalt. The water content, $n$, was not correctly determined due to the highly hygroscopic nature of the birnessite samples. We observed that the sample weight gradually increased when we exposed it to the atmosphere. We show the TG curve of non-Co in Fig. 2. In the heating process, we observed two weight loss steps, which began at 60 and 110 °C. The first step presumably corresponds to the removal of surface water, because there was no structural change in this temperature range. The second step can be assigned to the removal of the lattice water because the interlayer shrinks in this temperature range. According to Fig. 2, the Na-birnessite was completely dehydrated by 150 °C. The sample weight increased in the cooling process, suggesting that the dried Na-birnessite absorbed water.

Table 1
Chemical compositions of obtained samples

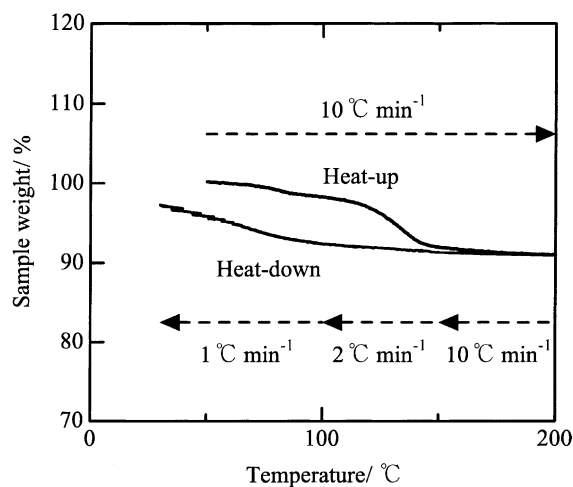| Sample | Chemical composition |
| --- | --- |
| Non-Co | $Na_{0.30}MnO_{1.95} \cdot nH_2O$ |
| 20-Co | $Na_{0.30}Mn_{0.83}Co_{0.17}O_{1.86} \cdot nH_2O$ |
| 30-Co | $Na_{0.37}Mn_{0.73}Co_{0.27}O_{2.00} \cdot nH_2O$ |
| 40-Co | $Na_{0.39}Mn_{0.64}Co_{0.36}O_{1.97} \cdot nH_2O$ |



Fig. 2. TG profile of non-Co. Arrows indicate direction and rate of heating (up/down).

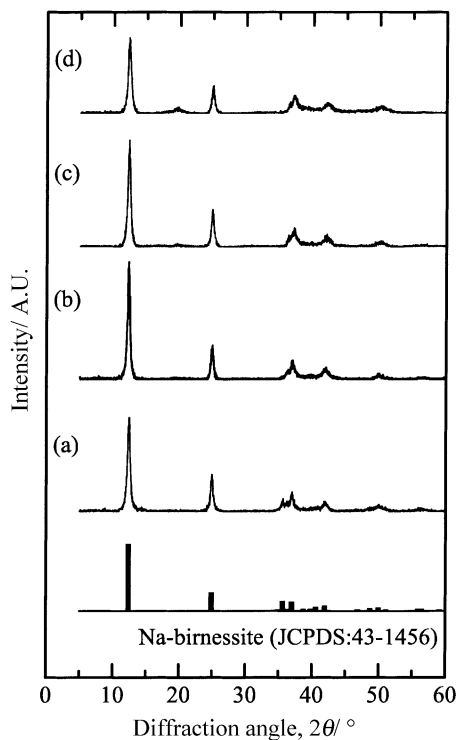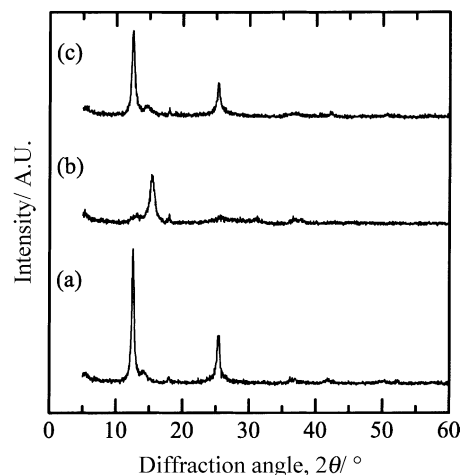Fig. 3. XRD patterns of: (a) non-Co; (b) 20-Co; (c) 30-Co; (d) 40-Co.



Fig. 4. XRD patterns of electrode pellets dried at: (a) 90 °C in air (AD sample); (b) 150 °C in a vacuum (VD sample); (c) room temperature in the electrolyte (EI sample).

These results suppose that Na-birnessite has high hygroscopicity. We estimated that the value of "*n*" was approximately 0.4 for the non-Co sample. For the sample substituted by cobalt, we obtained similar *n* values to non-Co.

Fig. 3 shows the XRD patterns of the obtained samples, together with the standard Na-birnessite pattern reported by Joint Committee on Powder Diffraction Standards (JCPDS). The XRD peaks of the obtained samples were successfully indexed using the standard pattern except for a small peak at 19.7° in Fig. 3c and d, which can probably be ascribed to some kinds of cobalt compound. The substituted samples maintained high crystallinity, regardless of the substitution ratios of 20, 30 and 40%.

We measured the XRD patterns and electrode performance of the non-Co samples dried under three different conditions, AD, VD and EI samples. Fig. 4 shows the XRD patterns of the electrode pellets. The AD sample had a pattern similar to the powder sample, and the layer distance was 7.0 Å. With the VD sample, we observed that the (0 0 1) peak shifted from 12.6 to 15.4° showing that the layer distance decreased from 7.0 to 5.7 Å. As the weight loss was associated with preparing the VD sample, we believe that this sample was dehydrated (see also Fig. 2). This layer distance of 5.7 Å is similar to that of $Na_{0.7}MnO_2$ (JCPDS 27-0752). The layer distance increased to 7.0 Å again when we exposed the VD sample to the ambient atmosphere. As Franger et al. have reported that Na-birnessite is obtained by treating $Na_{0.7}MnO_2$ with water [8], we think that the $MnO_2$ framework of VD sample is similar to that of $Na_{0.7}MnO_2$.

The EI sample had a pattern similar to the AD sample with the layer distance of 7.0 Å, suggesting that most of the lattice water was maintained in the interlayer.

Fig. 5 shows the discharge curves of these samples. We obtained a discharge capacity of 198 mAh g$^{-1}$ with the AD sample. However, in the charging process, we observed voltage fluctuation and lithium extraction seemed to be impossible. We were able to perform discharge–charge cycles with the VD sample, but its discharge capacity was small (150 mAh g$^{-1}$). For the EI sample, we obtained a large discharge capacity of 184 mAh g$^{-1}$, and we were also able to perform discharge–charge cycles.

We think the reason that we were unable to charge the AD sample was probably due to the water that remained on the sample surface. Chen et al. have reported that the layer distance of Na-birnessite decreased from 7.1 to 5.6 Å when they dehydrated this compound using a hot-press process at 150 °C to form electrode pellets [4]. This dehydrated Na-birnessite compound has a capacity of only 132 mAh g$^{-1}$. Their results correspond to our result for the VD sample. This suggests that the lattice water is required to obtain a large capacity. With the EI sample, we were able to perform discharge–charge cycles probably because the surface water was removed with the electrolyte immersion process. The capacity (184 mAh g$^{-1}$) was somewhat smaller than the first discharge capacity of the AD sample (198 mAh g$^{-1}$). We suppose that the large capacity of AD sample included the decomposition of surface water during the discharging process. These results show that we need to remove only the surface water and maintain the lattice water, in order to perform cycles with a large capacity.
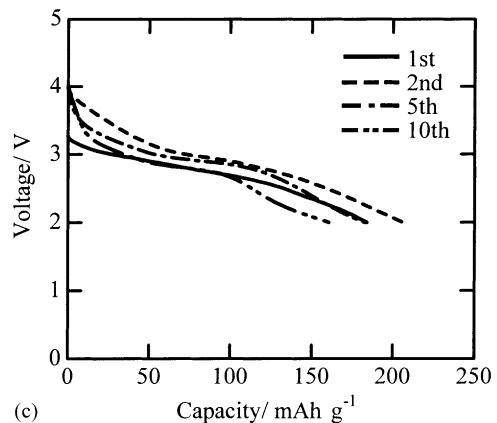
We measured the electrode performance of cobalt substituted EI samples. We were able to improve the cyclability by the cobalt substitution as shown in Fig. 6. From the discharge curves of 30-Co (Fig. 7), we also confirmed that the cobalt substituted sample had better cycling performance
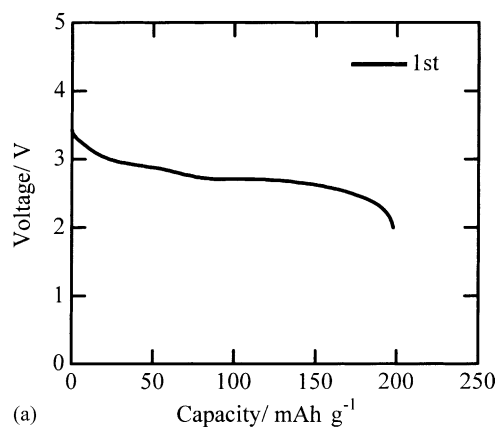
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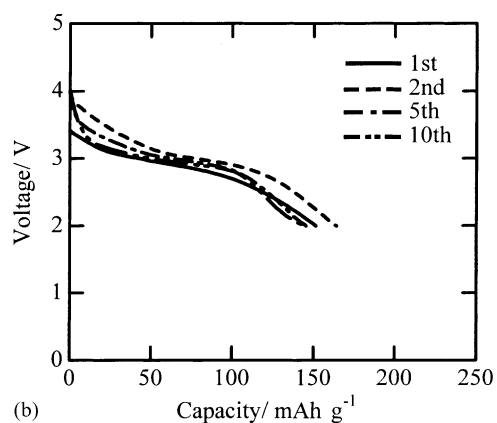


(b)



(c)

Fig. 5. Discharge profiles of: (a) AD sample; (b) VD sample; (c) EI sample at the 1st, 2nd, 5th and 10th cycle.
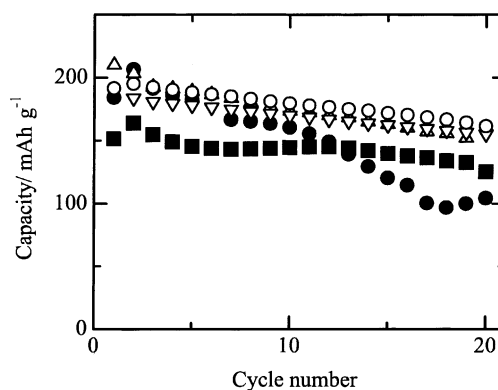


Fig. 6. Cyclability of cobalt substituted EI samples together with no substituted EI and VD samples (2.0–4.0 V, 0.1 mA cm$^{-2}$, room temperature). ($\triangle$): 20-Co; ($\bigcirc$): 30-Co; ($\triangledown$): 40-Co; ($\bullet$): non-Co; ($\blacksquare$): VD sample.
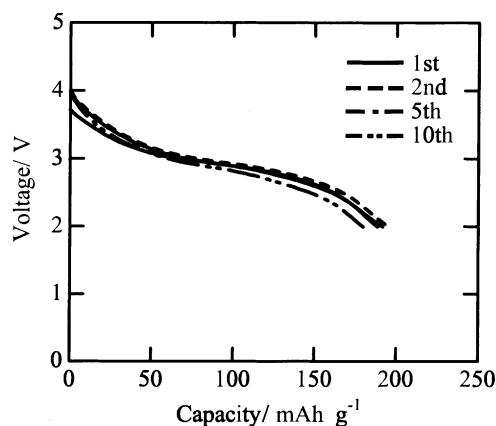


Fig. 7. Discharge profile of 30-Co at the 1st, 2nd, 5th and 10th cycle.

Nevertheless, the cobalt substitution was effective for improving the cycling performance, probably because the Co$^{3+}$ state is more stable than the Mn$^{3+}$ state. Other factors, such as enhanced conductivity [9] may also contribute to the improved cycling performance of the cobalt substituted birnessite.

## 4. Conclusions

A Na-birnessite sample dried only at 90 °C is hardly charged due to the surface water on the sample. With a sample dehydrated at 150 °C (VD sample), the layer distance considerably decreases to lose the lattice water, resulting in a small capacity. The lattice water is needed to maintain the layer distance and obtain a large capacity. The above results suggest that it is important to remove the surface water without losing the lattice water. We are able to obtain a large capacity of 184 mAh g$^{-1}$ and perform discharge–charge cycles with an EI sample prepared by an electrolyte immersion process. We improve the cyclability

than non-Co (Fig. 5c). Although the manganese ions are reduced and oxidized during cycling, we believe that the cobalt ions are always in the Co$^{3+}$ state, thus fixing the sodium ions in the interlayer and stabilizing the layer structure. It is also interesting that the initial capacity was nearly the same for samples with different cobalt content. This suggests that some of manganese ions in non-Co do not participate in the redox process. As the Na/Mn ratio in non-Co is about 0.3 (Table 1), we expect that 30% of the manganese exists presumably as Mn$^{3+}$ during discharge–charge cycles.

of the EI sample by partial cobalt substitution for manganese. The substituted cobalt is supposed to fix the sodium ions in the form of pillars and these maintain the layer structure. Trivalent substitute ions would have the same effect, and this bodes well for iron and aluminum substitution since these metals are less expensive than cobalt.

## Acknowledgements

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